

**LAID-OPEN PATENT GAZETTE**

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Title of the invention: Heat pressure curing adhesive for thinly sliced decorative timber sheets

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**Claim:**

A heat pressure curing adhesive for thinly sliced decorative timber sheets, comprising 100 parts by weight of the powder of the melamine methylation product or initial condensation product obtained by letting melamine and formaldehyde react with each other and 50 to 200 parts by weight of a thermoplastic resin emulsion as the resin content thereof.

## Detailed description of the invention:

[Industrial field of application]

The present invention relates to a novel heat pressure curing adhesive for thinly sliced decorative timber sheets. In more detail, the invention relates to a heat pressure curing adhesive for thinly sliced decorative timber sheets, which does not ooze to contaminate the surface of the thinly sliced decorative timber sheet<sup>and</sup> is excellent in adhesive strength, and little diffuses formalin.

[Prior art and problems thereof]

For the purpose of giving the attractive and decorative touch peculiar to natural wood to any surface, a thinly sliced decorative timber sheet is stuck to a plywood such as a general plywood, particleboard or fiberboard, and the plywood covered with the thinly sliced decorative timber sheet is used for furniture, walls, floors, ceilings, etc.

The thickness of the thinly sliced decorative timber sheet used for the plywood to be covered therewith is ~~as~~ very thick ~~as~~ - 0.1 mm to 0.2 mm<sup>^</sup> in view of the yield of the raw wood, but on the other hand, in view of the demand for high quality, thinly sliced decorative timber sheets with a thickness of 0.5 mm or more are also increasingly used. In the former case, the ooze contamination by the adhesive on the surface of the thinly sliced decorative timber sheet is liable to occur. Further in the latter case, since the contraction stress and expansion stress of the thinly sliced decorative timber sheet are large, a high adhesive strength is

required. Further, the plywood covered with a thinly sliced decorative timber sheet used for cupboards is required to be very small in the amount of formalin diffused from the adhesive.

The conventional heat pressure curing adhesives used for thinly sliced decorative timber sheets include a water dispersible urea resin, a urea-melamine co-condensation resin and mixtures such as vinyl acetate emulsion and synthetic rubber latex. Moreover, a mixture consisting of the powder of the melamine methylation product or initial condensation product obtained by letting melamine and formaldehyde react with each other (hereinafter briefly called the powder melamine resin) and polyvinyl alcohol is also used. However, these adhesives are not satisfactory in view of the prevention of ooze contamination and adhesive strength.

[Means for solving the problems]

The present inventors made an intensive study to solve these problems, and as a result, <sup>they</sup> <sub>A</sub> arrived at a heat pressure curing adhesive for thinly sliced decorative timber sheets, which does not ooze to contaminate the surface of a thinly sliced decorative timber <sub>and</sub> sheet <sub>A</sub> has a high adhesive strength, <sup>and</sup> <sub>A</sub> is very small in the amount of formalin diffused, and shows viscous flowability to assure excellent working convenience.

This invention provides a heat pressure curing adhesive for thinly sliced decorative timber sheet, comprising 100 parts by weight of the powder of the melamine methylation product or initial condensation product obtained by letting melamine and formaldehyde react with each other and 50 to 200 parts by weight

of a thermoplastic resin emulsion as the resin content thereof. Further, in this invention, as required, adequate amounts of a thickener, filler and curing accelerator can also be added to the adhesive.

The powder melamine resin used in this invention refers to the powder of the melamine methylation product or initial condensation product obtained, for example, by mixing 1 mole of melamine and 2 to 6 moles of formaldehyde, heating the mixture at pH 7 or more, for reaction, and spray-drying. Meanwhile, a so-called melamine co-condensation product in which melamine is partially substituted by urea, benzoguanamine, phenol or resorcin, etc. can also be used.

Further, as formaldehyde, generally formalin is used. However, paraformaldehyde or methylformalin that can react substantially as formaldehyde can also be used.

A thermoplastic resin emulsion means a general aqueous dispersion of a natural or synthetic polymer. Particularly usable is an aqueous dispersion obtained by polymerizing one selected from styrene, butadiene, acrylic acid ester, methacrylic acid ester, acrylonitrile, chloroprene, isoprene, isobutene, vinyl acetate, ethylene, vinyl chloride, vinylidene chloride, or copolymerizing two or more copolymerizable ones selected from the foregoing, or a natural rubber emulsion. A modifying monomer can also be partially copolymerized. As the modifying monomer having a carboxyl group, enumerated are acrylic acid, methacrylic acid, itaconic acid, maleic acid, etc., and anhydrides such as itaconic

anhydride and maleic anhydride. As the modifying monomer having an N-methylol group, enumerated are N-methylolacrylamide and N-methylolmethacrylamide. As the modifying monomer having a glycidyl group, enumerated are glycidyl acrylate and glycidyl methacrylate. As the modifying monomer having a hydroxyl group, enumerated are allyl alcohol, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate and 2-hydroxypropyl methacrylate. As the modifying monomer having an amino group, enumerated are N,N-dimethylaminoethyl acrylate, vinylpyridine and tert-butylaminoethyl methacrylate. As the modifying monomer having an amide group, enumerated are acrylamide, methacrylamide and maleinamide. Preferred are styrene-butadiene copolymer and methacrylic acid ester-butadiene copolymer.

As the mixing ratio of the thermoplastic resin emulsion and the powder melamine powder of this invention, it is necessary to use 50 to 200 parts by weight, preferably 80 to 180 parts by weight of the thermoplastic resin emulsion as the resin content per 100 parts by weight of the powder melamine resin. Meanwhile, the resin content means the residue remaining after removing the volatile water from the emulsion. As a particular measuring method, 1 to 2 g of an emulsion is placed on an aluminum plate and dried at 105°C for 3 hours, and the resin content is calculated from the balance.

If the amount of the thermoplastic resin emulsion is smaller than 50 parts by weight, the ooze contamination on the surface of the thinly sliced decorative timber sheet occurs. If the amount is larger than 200 parts by weight, the adhesive strength resisting

hot water and resisting boiled water of the adhesive declines, and the viscous flowability assuring good working convenience cannot be obtained.

Furthermore, a thickener such as methyl cellulose, carboxymethyl cellulose sodium salt or polyvinyl alcohol and a filler such as wood flour, clay, calcium carbonate, talc, starch or water can also be added to the adhesive of this invention. For accelerating the curing of melamine resin, ammonium chloride, paratoluenesulfonic acid or hydrochloric acid, etc. can also be added.

#### [Examples]

Examples and comparative examples of this invention are described below.

#### [Example 1]

One hundred parts by weight of powder trimethylolmelamine (trade name Nicaresin 305 produced by Nippon Carbide Industries Co., Ltd.), 200 parts by weight of styrene-butadiene copolymer emulsion (trade name POLYLAC 750 produced by Mitsui Toatsu Kagaku, resin content 50%) as a thermoplastic resin emulsion, 200 parts by weight of wheat flour, 5 parts by weight of methyl cellulose and 330 parts by weight of water were mixed to obtain an adhesive, that was subjected to the following tests.

#### (Adhesive strength)

Three-ply plywoods were prepared. They were subjected to the ordinary adhesive strength test, hot and cold water immersion test and boiling test of <sup>the</sup> Japanese Agricultural Standards (in the boiling

test, the sample was immersed in boiled water for 4 hours and then immersed in water of room temperature till it was cooled, and subjected to an adhesive strength test in the wet state, without being subjected to hot/cold cycles).

For preparing a 3-ply plywood, a 1.4 mm thick red lauan veneer was used. For each adhesive layer, the adhesive was applied by 15 g/shaku<sup>2</sup> (shaku = 30.3 cm), and the plywood was thermally clamped at a temperature of 110°C at a pressure of 10 kg/cm<sup>2</sup> for 1 minute 30 seconds.

(Ooze contamination)

A 2.5 mm thick 3-ply plywood was coated with the adhesive by 10 g/shaku<sup>2</sup>, and a 0.2 mm thick straight-grained Japanese oak (*Quercus serrata*) as a thinly sliced decorative timber sheet was placed on it. The laminate was thermally clamped at a temperature of 110°C at a pressure of 5 kg/cm<sup>2</sup> for 1 minute, to obtain a specimen. Whether ~~or not~~ the adhesive oozed to contaminate the surface of the thinly sliced decorative timber sheet of the specimen was confirmed. No ooze contamination was determined to be good.

[Example 2]

An adhesive was obtained and subjected to tests according to the same methods as described in Example 1, except that the added amount of the styrene-butadiene copolymer emulsion as the thermoplastic resin emulsion was 120 parts by weight.

[Example 3]

An adhesive was obtained and subjected to tests according to the same methods as described in Example 1, except that methyl

methacrylate-butadiene copolymer emulsion (trade name POLYLACK 707 produced by Mitsui Toatsu Kagaku, resin content 50%) was used as the thermoplastic resin emulsion.

[Comparative Example 1]

An adhesive was obtained and subjected to tests according to the same methods as described in Example 1, except that the amount of the styrene-butadiene copolymer used as the thermoplastic resin emulsion was 80 parts by weight.

[Comparative Example 2]

An adhesive was obtained and subjected to tests according to the same methods as described in Example 1, except that the added amount of the styrene-butadiene copolymer emulsion as the thermoplastic resin emulsion was 500 parts by weight.

[Comparative Example 3]

An adhesive was obtained and subjected to tests according to the same methods as described in Example 1, except that no thermoplastic resin emulsion was added.

[Comparative Example 4]

An adhesive was obtained and subjected to tests according to the same methods as described in Example 1, except that the added amount of the powder methylolmelamine was 150 parts by weight and that no thermoplastic resin emulsion was added.

[Comparative Example 5]

An adhesive was obtained and subjected to tests according to the same methods as described in Example 1, except that the added amount of the powder methylolmelamine was 200 parts by weight and



that no thermoplastic resin emulsion was added.

[Comparative Example 6]

An adhesive was obtained and subjected to tests according to the same methods as described in Example 1, except that the added amount of the styrene-butadiene copolymer emulsion as the thermoplastic resin emulsion was 400 parts by weight.

Table 1

		Trimethylol-melamine	PL-750	PL-707	Wheat flour	Methyl cellulose	Water
Example	1	100	200	0	200	5	330
	2	100	120	0	200	5	330
	3	100	0	200	200	5	330
Comparative Example	1	100	80		200	5	330
	2	100	500		200	5	330
	3	100	0		200	5	330
	4	150	0		200	5	330
	5	200	0		200	5	330
	6	100	400	0	200	5	330

The results the abovementioned tests are shown in Table 2.

In Table 2, in each box of adhesive strength, the numeral on the left side shows an adhesive strength (kg/cm<sup>2</sup>), and the numeral on the right side shows a wood failure rate.

Table 2

		Example			Comparative Example					
		1	2	3	1	2	3	4	5	6
Adhesive strength	Ordinary adhesive strength	20.6-100	18.6-100	21.0-100	19.4-100	17.4-92	18.6-100	19.1-100	21.9-100	15.3-84
	Hot and cold water resistance	11.5-17	9.5-2	12.0-8	13.2-20	5.7-0	13.9-25	14.6-35	15.8-46	8.1-12
	Boiling resistance	4.7-0	2.2-0	4.4-0	5.3-0	Peel	4.8-0	5.9-0	7.8-5	2.0-0
Ooze contamination		Good	Good	Good	Poor	Good	Poor	Poor	Poor	Good

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⑮ 発明の名称 熱圧硬化型木質系突板化粧加工用接着剤

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## 明 細 書

## 1. 発明の名称

熱圧硬化型木質系突板化粧加工用接着剤

## 2. 特許請求の範囲

メラミンとホルムアルデヒドを反応させて得られるメラミンのメチロール化物または初期縮合物の粉末100重量部と、熱可塑性樹脂エマルジョンを樹脂分で50～200重量部含有してなることを特徴とする熱圧硬化型木質系突板化粧加工用接着剤。

## 3. 発明の詳細な説明

(産業上の利用分野)

本発明は、新規な熱圧硬化型木質系突板化粧加工用接着剤に関する。詳しくは、突板表面における接着剤のしみ出し汚染を生ぜず、優れた接着力を有し、しかも、放散ホルマリン量の非常に少ない熱圧硬化型木質系突板化粧加工用接着剤に関するものである。

(従来の技術とその問題点)

従来、表面に木材質特有の美観を目的として、一般合板、パーティクルボード、ファイバーボ-

ード等の如き木質加工合板上に突板単板を貼り合わせたもの、即ち突板化粧加工したものは、突板化粧加工製品として家具、壁、床材あるいは天井板等に供されている。

突板化粧加工製品に用いられる突板単板の厚さは最近原木の歩止り向上の観点から、0.1mm～0.2mmと極めて薄い突板単板を使用したりする一方で、高級感指向より0.5mm以上の厚い突板単板を使用する場合が増加してきている。前者の場合、使用した接着材の突板表面へのしみ出し汚染がますます発生しやすくなる実情にある。また後者の場合、突板の収縮、膨張応力が大きいため、高強度の接着力が要求されて来ている。又食器棚のような突板化粧加工製品に対しては、放散ホルマリン量の非常に少ないものが要求されている。

従来、熱圧硬化型木質系突板化粧加工用接着剤として水分散型尿素樹脂又は尿素・メラミン共重合樹脂の単独又は酢酸ビニルエマルジョン、合成ゴムラテックス等の混合物が使用されている。また、メラミンとホルムアルデヒドを反応させて得

られるメラミンのメチロール化物または初期縮合物の粉末（以下、粉末メラミン樹脂と略称）とポリビニルアルコールの混合物も使用されているが、しみ出し汚染の防止、接着力に未だ満足しうるものではない。

（問題点を解決する為の手段）

本発明者等はこれらの諸問題を解決すべく鋭意研究を重ねた結果、上記した如き突板表面におけるしみ出し汚染性がなく、高い接着力を有し、放散ホルマリン量が非常に少なく、しかも、ねばりのある流動性を示す優れた作業性が得られる熱圧硬化型木質系突板化粧加工用接着材を提供することができに到った。

即ち本発明はメラミンとホルムアルデヒドを反応させて得られるメラミンのメチロール化物または初期縮合物の粉末 100重量部と、熱可塑性樹脂エマルジョンを樹脂分で50～200重量部を含有してなることを特徴とする熱圧硬化型木質系突板化粧加工用接着剤である。さらに本発明においては必要に応じ適量の増粘材、充填材および硬化促進剤

を含有していてもよい。

本発明において使用する粉末メラミン樹脂はメラミン1モルに対しホルムアルデヒド2～6モルを配合し、pH7以上で加熱させ、反応後スプレー乾燥などの方法で粉末状となしたメラミンのメチロール化物または初期縮合物と言われるものである。なおメラミンの一部を尿素、ベンゾグアナミン、フェノール、レゾルジンなどに置き換えた、いわゆるメラミン共縮合物を使用しても差し支えない。

またホルムアルデヒドは一般的にホルマリンを用いるが、このほかパラホルムアルデヒドまたはメチルホルマリンのごとき実質的にホルムアルデヒドとして反応するものを使用しても差し支えない。

熱可塑性樹脂エマルジョンとは一般に天然あるいは合成高分子の水性分散液を意味し、具体的にはスチレン、ブタジエン、アクリル酸エステル、メタアクリル酸エステル、アクリルニトリル、クロロブレン、イソブレン、イソブテン、酢酸ビニ

ル、エチレン、塩化ビニル、塩化ビニリデンなどから選ばれた1種又は共重合可能な2種以上を共重合した水性分散液又は天然ゴムエマルジョンがある。変性モノマーを一部共重合してもよい。変性モノマーとしてはカルボキシル基を有するものとしてアクリル酸、メタアクリル酸、イタコン酸、マレイン酸等、酸無水物として無水イタコン酸、無水マレイン酸、N-メチロール基を有するものとしてN-メチロールアクリルアミド、N-メチロールメタアクリルアミド等、グリシジル基を有するものとしてグリシジルアクリレート、グリシジルメタアクリレート等、水酸基を有するものとしてアリルアルコール、2-ヒドロキシエチルアクリレート、2-ヒドロキシプロピルアクリレート、2-ヒドロキシプロピルメタアクリレート等、アミノ基を有するものとしてN,N-ジメチルアミノエチルアクリレート、ビニルピリジン、tert-ブチルアミノエチルメタアクリレート等、アミド基を有するものとしてアクリルアミド、メタアクリルアミド、マレインアミド等があげられ

る。好ましくはスチレン、ブタジエン共重合体、メタアクリル酸エステル、ブタジエン共重合体が良い。

本発明の熱可塑性エマルジョンと粉末メラミン樹脂との混合比率は樹脂分換算で粉末メラミン樹脂100重量部に対し熱可塑性樹脂エマルジョンは50～200重量部、好ましくは80～180重量部であることが必要である。なお樹脂分とはエマルジョンから揮発性水分を取り除いたものを意味し、具体的測定法としては1～2gのエマルジョンをアルミ皿にとり、105℃3時間乾燥した残量より換算する。

熱可塑性エマルジョンが50重量部より少ない場合、本発明の目的である突板表面におけるしみ出し汚染が発生し、200重量部より多い場合、耐温水、耐煮沸水接着力が低下すると共にねばりのある作業性が良好な接着剤が得られない。

又本発明による接着剤にメチルセルロース、カルボキシメチルセルロースナトリウム塩、ポリビニルアルコール等の増粘剤や小麦粉、木粉、クレ

一、炭酸カルシウム、タルク、澱粉、水等の充填剤、増粘剤を添加し使用することに支障はない。メラミン樹脂硬化を促進させるために塩化アンモニウム、パラトルエンスルホン酸、塩酸等を添加してもよい。

〔実施例〕

以下に本発明の実施例及び比較例を示す。

実施例 1

粉末メラミチロールメラミン（商品名ニカレジ-305 日本カーバイト工業製）100重量部に対し熱可塑性エマルジョンとしてスチレン、ブタジエン共重合体エマルジョン（商品名ポリラック 750 三井東圧化学製、樹脂分50%）を 200重量部、小麦粉を 200重量部、メチルセルロースを 5重量部、水を 330重量部添加混合し接着剤を得、下記の試験に供した。

（接着力評価）

3 プライ合板を作成し、日本農林規格普通合板の常態接着力試験、温冷水浸せき試験、煮沸試験（ただし煮沸試験は繰返しを行わず沸とう水中に

4 時間浸せきした後、室温の水中にさめるまで浸せきし、ぬれたままの状態接着試験を行った）に依り接着力評価を行った。

3 プライ合板作成は、1.4mm 厚のレッドラワン単板を使用し各接着層が 15g/ 尺<sup>2</sup> となるよう接着剤を塗布し、110℃の温度 10Kg/cm<sup>2</sup>の圧力で 1分30秒熱圧縮した。

（しみ出し汚染性評価）

2.5mm 厚の 3 プライ合板上に塗布量 10g/ 尺<sup>2</sup> 接着剤を塗布し、その上に 0.2mm の桎目ナラの突板を乗せ 110℃の温度、5Kg/cm<sup>2</sup>の圧力で 1分間熱圧縮し試験体を得た。試験体の突板表面に接着剤のしみ出し汚染の有無を確認し無いものを良と示した。

〔実施例 2〕

熱可塑性エマルジョンとしてスチレン、ブタジエン共重合エマルジョンの添加量を 120重量部とした事以外実施例-1と同じ方法で接着剤を得、試験に供した。

〔実施例 3〕

熱可塑性エマルジョンとしてメチルメタアクリレート、ブタジエン共重合エマルジョン（商品名ポリラック 707 三井東圧化学製 樹脂分50%）を使用する事以外実施例-1と同じ方法で接着剤を得、試験に供した。

（比較例 1）

熱可塑性エマルジョンとしてスチレン、ブタジエン共重合エマルジョンの添加量を 80重量部とした事以外実施例 1 と同じ方法で接着剤を得、試験に供した。

（比較例 2）

熱可塑性エマルジョンとしてスチレン、ブタジエン共重合エマルジョンの添加量を 500重量部とした事以外実施例 1 と同じ方法で接着剤を得、試験に供した。

以上の結果を表 1 にまとめて示した。

表 1 中、接着力の表示は左側が接着力 (kg/cm<sup>2</sup>)、右側が木破率を表す。

表 1

		実施例 1	実施例 2	実施例 3	比較例 1	比較例 2
接 着 力	常 体	20.6-100	18.6-100	21.0-100	19.4-100	17.4-92
	温冷水	11.5-17	9.5 - 2	12.0-8	13.2-20	5.7-0
	煮沸水	4.7-0	2.2 - 0	4.4 - 0	5.3-0	ハクリ
しみ出し汚染性		良	良	良	不良	良